

PATENT SPECIFICATION

NO DRAWINGS

1,106,920

1,106,920



Date of Application and filing Complete Specification: 7 Dec., 1966.
No. 54819/66.

Application made in United States of America (No.516,086) on 23 Dec., 1965.
Complete Specification Published: 20 March, 1968.
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Index at acceptance:—C3 P(2A, 2C6A, 2C8C, 2C11, 2C13B, 2D1A, 2K7, 2T2A); B7 C3B9;
C3 Q(A, C6A, C8C, C11, D1A, T2A)

Int. Cl.:—C 08 d 13/16

COMPLETE SPECIFICATION

Polyester-Fiber-Reinforced Elastomeric Articles

We E. I. DU PONT DE NEMOURS & COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware,

5 United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to novel cord reinforced elastomeric articles, and more particularly, to polyester fiber reinforced rubber articles having improved resistance to degradation.

15 Although polyester - fiber - reinforced elastomeric structures offer advantages over equivalent nylon- or rayon-reinforced structures, wide-spread acceptance of some polyester-reinforced articles, such as pneumatic tires, has been limited by the strength loss and by the adhesion loss experienced under extreme service conditions. Attempts to improve the performance of polyester-reinforced elastomeric articles by various means, such as by changing 20 the composition of the elastomer, have met with only limited success. Further improvement is needed.

25 The present invention provides novel and useful polyester - fiber - reinforced elastomeric articles which give superior service under extreme service conditions, particularly with respect to strength loss and adhesion loss.

30 It has now been found that polyester - fiber-reinforced elastomeric articles of improved performance are obtained if the elastomer is characterized by high moisture permeability, and is free of accelerators which are amines or which are capable of breaking down into amines or amine free radicals upon exposure to elevated temperatures.

35 Therefore, in accordance with the present invention, we provide a composite structure comprising an elastomeric article having incorporated therein reinforcing fibers prepared from a synthetic linear condensation polyester

50 wherein the elastomer is characterized by moisture permeability of at least 20 gms. per square meter per 24 hours, when measured by the procedure described herein, and where the elastomer is substantially free of accelerators which are amines or compounds capable of generating amines when heated as in vulcanization.

55 The advantages of the structure provided by this invention become most apparent when the structure is in the form of a pneumatic tire which is subjected to heavy loads at high speeds.

60 By "synthetic linear condensation polyester" we mean a high molecular weight polymer composed of predominantly hydrocarbon

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—C—O—
65 units connected by ester groups, —C—O—, in the main chain of the molecule. Such polyesters are described, for example in U.S. Specification No. 2,465,319, and the best-known commercial example is polyethylene terephthalate, which will be used in the examples to illustrate the invention.

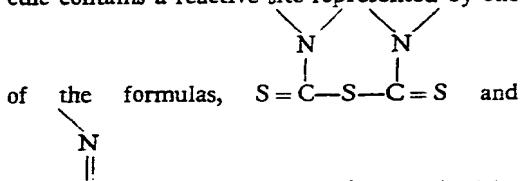
70 By "moisture permeability" is meant the rate of transmission of water vapor through a sheet of the elastomer under standardized test conditions. The test for Measuring Water Vapor Transmission of Materials in Sheet Form, ASTM designation E96-53T, is used. Water vapor transmission is measured through a sheet of elastomer having a thickness of 80 mils (2 mm.) at 100°F. (37.8°C.) with a relative humidity on one side of the sheet of 100% and on the other side 0%. Elastomer samples are compounded, shaped, cured for 40 minutes at 300°F. (148°C.), and tested within 48 hours. Suitable elastomers are those which give a water vapor transmission value of at least 20 gms. per square meter per 24 hours in this test.

75 80 85 Moisture permeability of elastomers is a function of many variables, among which the most important are the type of elastomer or

elastomer blend and the amount of each component in the blend. Other factors affecting permeability are the method of preparation of the elastomer, the amount and type of oil loading, the amount and type of carbon black loading, and the state of cure of the elastomer. The effects of these variables on permeability are mere matters of skill in the art and have been described in the literature, as for example by Iyengar *Polymer Letters*, Vol. 3, page 663 (1965).

The highest values for moisture permeability have been observed in rubber compounds comprising cis - 1,4 - polybutadiene. Therefore, the preferred elastomer for use in the present invention is one which contains at least 50% by weight cis - 1,4 - polybutadiene. The remainder of the elastomer stock may be derived from other sources such as natural rubber or styrene-butadiene rubber. The preparation and properties of cis - 1,4 - polybutadiene are described in U.S. Specification No. 3,178,402.

It is essential that the elastomer stock used in the present invention be substantially free of accelerators which are amines or amine-forming compounds. Such accelerators are found to markedly increase both strength loss and adhesion loss in the ultimate elastomeric structure under severe use conditions. Suitable accelerators are those in which the molecule contains a reactive site represented by one



35 and is further characterized by being free of sulfur - to - nitrogen bonds. Suitable accelerators may be chosen, for example, from the thiiazoles having no amine components. Such compounds include 2,2'-dithiobis(benzothiazole), benzothiazole - 2 -

thiol, and the zinc salt of benzothiazole - 2 - thiol. Other suitable accelerators include tetraethylthiuram monosulfide and other tetraalkylthiuram monosulfides.

Accelerators which are *not* suitable for use in the elastomeric structure of this invention include the aryl substituted guanidines, aldehyde-amine condensation products, dithiocarbamates, thiuram disulfides, and benzothiazole sulfenamides. Some specific examples of commonly used accelerators which are not suitable are 2 - (morpholinothio) - benzothiazole, N - cyclohexylbenzothiazole - 2 - sulfenamide, N,N - diisopropylbenzothiazole - 2 - sulfenamide, N - tert - butylbenzothiazole - 2 - sulfenamide, piperidinium pentamethylene-dithiocarbamate and tetramethylthiuram disulfide. None of the compounds in this group are suitable because they have the potential of splitting out an amine or amine free radical under vulcanization conditions.

The improvement provided by the present invention is not dependent upon the adhesive used to bond the fibers or cord to the elastomer. Of course, an adhesive suitable for use on polyester structures should be used, and a number of these are known in the art. Suitable adhesives are shown in the examples below.

Where the term "skim stock" is used herein, reference is made to the compounded elastomeric material used in the preparation of reinforcement plies. Skim stock is used contiguous to the reinforcement cords or similar structures.

This invention will be more readily understood by reference to the following examples which are intended to be illustrative and not limitative. Unless otherwise indicated, parts and percentages are by weight.

EXAMPLE I

Three 8.50-14 pneumatic tires (Tires A, B and C), with 4 bias plies, are constructed with polyester cords. The composition of the skim stock is specified in Table 1.

TABLE 1
Skim Stock Formulation

Ingredient	Parts by Weight
cis-1,4-polybutadiene rubber	75
Natural rubber	25
FEF black	35
Circosol 2XH (a medium viscosity processing oil)	8
Rosin oil	2
Zinc Oxide	5
Sulfur	2.5
2,2'-dithiobis(benzothiazole) accelerator	.1
Stearic acid	2
Antioxidant (25% di-p-methoxy-diphenylamine, 25% diphenyl-p-phenylene-diamine, 50% phenyl-beta-naphthylamine)	1
Total of ingredients	156.5

5 These ingredients are combined on a rubber mill. The natural rubber is added to the cis-1,4 - polybutadiene rubber in the mill at 25°C.; then the oils are added, followed by the antioxidant and all the other ingredients, with the accelerator being added last. This elastomer stock is found to have a moisture permeability of 34 gms. per square meter per 10 hours.

10 The cords are formed of poly(ethylene terephthalate) yarns and are of 840/1/2 construction twisted 12Z turns in the ply and 12.5S turns in the cord. This greige cord is dipped 15 in an aqueous adhesive subcoating mixture, described below, and heated in an oven for 1 minute at 425°F. (219°C.) under an applied stretch of 7%. Then the cord is dipped again, this time in a resorcinol-formaldehyde/rubber latex (RFL) coating described below, and heated again in an oven for 1 minute at 425°F. with an applied stretch of 0.5%. The dipped cord has 3.98% total dip pickup, and an observed denier of 1784.

20 The aqueous adhesive subcoating is prepared by mixing 400 ml. of water, 0.4 ml. of an alkylarylpolyether alcohol nonionic dispersing agent, and 16.0 gms. of powdered phenol-blocked methylene - bis(4 - phenylisocyanate) and milling to a fine dispersion. This dispersion is then thickened with 25.0 ml. of a 0.5% by weight solution of a high molecular weight diethylaminoethyl methacrylate polymer

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as the acetate salt, and then mixed with 4.8 ml. of a liquid polyepoxide formed from glycerol and epichlorohydrin and having a molecular weight of about 310 and an epoxy value of 0.67 equivalent per 100 gms.

30 The RFL coating is prepared by mixing 1.38 parts of resorcinol, 2.02 parts of 37% formaldehyde, 2.39 parts of 1.6% aqueous sodium hydroxide, and 27.8 parts water. This mixture is aged for six hours at 75—78°F. and then added to a mixture of 30.5 parts of 41% solids butadiene/styrene/vinylpyridine (70/15/15) copolymer latex diluted with 7.64 parts water and 1.42 parts 28% ammonium hydroxide. The final mixture is allowed to age for 12 hours before using.

35 Plies for each pneumatic tire are made by conventional techniques from the dipped cords and the skim stock of Table 1. Three 8.50—14 pneumatic tires with 4 bias-cut plies each are prepared, with tread, sidewalls and inner-liner having the same stock composition as the skim stock. Forming and vulcanization of each tire is done in conventional equipment and by conventional techniques.

40 Tire A is exercised for 3,000 miles (4820 km.) at speeds up to 75 m.p.h. (120.5 km./hr.) in a High Speed Endurance Wheel Test, as described in the *Transactions of the ASME*, Vol. 82 (1960), Series B, No. 1, pages 23 to 38. During this test the temperature contained inside the tire rises to 196°F. (91°C.).

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Tire B is heated in an oven at 325°F. (163°C.) for 24 hours. Tire C is a control.

After these tests each tire is dissected, and the cords from each of the three tires are

observed to retain a rubber covering, indicating that adhesion is good. Lengths of cord from each tire are tested for tensile strength, with the results shown in table 2.

TABLE 2

Break Strength of Cords Removed from Tires

	Av. Strength, Kg.
Tire A (Exercised Tire)	12.6
Tire B (Heat-aged Tire)	11.0
Tire C (Control Tire)	12.7

10 The data show that the strength loss of the exercised tire is essentially zero, and that of the heated tire is about 12%.

15 Tire B₁, similar to Tire B but prepared from an elastomer containing, instead of the 2,2'-dithiobis(benzothiazole), 1 part per hundred parts of rubber of 2-(morpholinothio)-benzothiazole 2-sulfenamide (an accelerator conventionally used for nylon-reinforced tires), experiences a 39% strength loss after being heated in an oven at 325°F. (163°C.) for 24 hours. Furthermore, adhesion of cord to rubber in Tire B₁ is poor.

20 EXAMPLE II
25 This example illustrates the effect of using an elastomer stock having an insufficient moisture permeability.

30 Three additional tires (Tires D, E and F) are built identical to Tires A, B and C of Example I, except that the mixture of cis-1,4-polybutadiene rubber and natural rubber are replaced with 100 parts of styrene-butadiene rubber. The accelerator used is 2,2'-dithiobis(benzothiazole). The moisture permeability of this elastomer stock is 8 gms. per

square meter per 24 hours. Tire D is exercised in the same manner as Tire A, and Tire E is heated as was Tire B. Tire F is the control for Tires D and E. On dissection, the cords from Tire D show a light white band in the shoulder, and cords from Tire E show slightly white throughout, showing that adhesion retention is poor in both tires. The strength loss of cords removed from exercised Tire D is 8%, and of cords from heated Tire E is 11%, which is comparable to that of Tires A and B of Example I.

EXAMPLE III
50 This example illustrates the effect of using an elastomer which has a low moisture permeability and which also contains an unsuitable accelerator.

55 Three additional tires (Tires G, H and I) are built identical to Tires A, B and C of Example I except for rubber stock formulations. The skim and innerliner is as specified in Table 3. This is a skim stock typical of those used in the tire industry and has a moisture permeability of 8 gms. per square meter per 24 hours. The tread stock is conventional.

TABLE 3
Conventional Skim Stock Formulation

Ingredient	Parts by Weight
Styrene-butadiene rubber	50.0
Natural rubber	50.0
High-abrasion-furnace carbon black	35.0
Naphthenic oil (a medium viscosity processing oil)	10.0
Zinc Oxide	3.0
Stearic Acid	1.0
Antioxidant (Polymerized trimethyl dihydroquinoline)	1.0
2-(morpholinothio)-benzothiazole	1.25
2,2-dithiobis(benzothiazole)	0.25
Sulfur	2.50
Total of Ingredients	154.0

5 Tire G is exercised in the High Speed Endurance Test, described for Tire A in Example I. However, Tire G fails prematurely at 1300 miles with the contained air temperature rising to 243°F. (118°C.).

10 Tire H is heated as is Tire B of Example I, and Tire I is the control for Tires G and H.

15 On dissection, the cords of Tire G have a severe white band in the shoulder, and Tire H has white (rubber free) cords throughout, showing that adhesion retention is very poor in both Tires G and H. Furthermore, the cord strength loss of the heated tire is 44%.

20 The results of the above three examples show that both a suitable accelerator and a synthetic elastomer having a high moisture permeability are necessary to obtain and retain good cord-to-rubber adhesion as well as to retain cord strength in polyester-fiber-reinforced structures. The tires in these examples, which are prepared from low-moisture-permeability rubber, are unsatisfactory in having poor adhesion retention whether or not a suitable accelerator is present. Likewise, Tire B, with high-moisture-permeability rubber but with an unsuitable accelerator is also unsatisfactory in having high strength loss as well as poor adhesion.

30 **EXAMPLE IV**

This example quantitatively shows the adhesion retention of polyester-reinforced elastomeric articles prepared according to this invention.

35 Laboratory 2-ply pad-test samples are prepared by incasing two layers of side-by-side dipped polyester cords, as prepared for Example I, in about 1/4-inch (6.4 mm.) thickness of elastomer stock specified above in Table 1; about 1/32-inch (0.8 mm.) thickness of this stock separates the two cord layers. This combination is further incased in the elastomer stock specified in Table 3 so that the total thickness of the article is 0.8 inch (20.3 mm.).

40 Four of such articles (articles a, b, c and d) are cured in an oven at 300°F. (150°C.) for 60 minutes. Three of these cured articles (b, c and d) are then aged in a heated oven at temperatures and for times specified in Table 4, while cured article "a" is kept aside as a control. For testing, all excess rubber is removed from each article to leave a one-inch (2.54 cm.) wide 2-ply strip just covered with rubber, and with an end of each cord layer available for clamping.

45 50 Identical cords are similarly encased in another rubber, but this time all of the rubber is as specified in Table 3, to provide four articles (articles e, f, g and h), each article being of 0.8-inch (20.3 mm.) thickness. Each article is cured and articles f, g and h are heated in the same manner as articles b, c and d.

55 60 65 For further comparison, 6,6 nylon cords of 840/1/2 construction, twisted 10 Z turns in the ply and 10 S turns in the cord, are similarly tested. The greige cord is dipped in the RFL coating mixture of Example I and

heat-stretched conventionally. The observed denier is 1788. These cords are used to provide articles i, j, k and l, identical to articles e, f, g and h except for the cord used. Articles i, j, k and l are cured and heated in the same manner as articles a, b, c and d.

Dipped nylon cords, as specified above, are also used to provide articles m, n, o and p, which are incased, cured and heated as are

articles a, b, c and d.

Each of these 16 articles is tested for adhesion retention by measuring the force in pounds required to pull apart, for a cord length distance of 1-1/2 inch (38.1 mm.), the two-cord layers in one article. Table 4 shows the results of this test. The cords are pulled apart cold at 25°C. and hot at 140°C.

TABLE 4
Adhesion Retention of Cords Incased in Rubber

Article	Cord	Rubber	Treatment	Stripping Force in lbs.	
				Cold	Hot
a	polyester	Tables 1-3	*	74	53
b	"	"	**	87	52
c	"	"	***	73	43
d	"	"	****	55	36
e	"	Table 3	*	68	59
f	"	"	**	42	32
g	"	"	***	28	23
h	"	"	****	18	6
i	nylon	Table 3	*	74	46
j	"	"	**	64	32
k	"	"	***	66	41
l	"	"	****	56	33
m	"	Tables 1-3	*	70	48
n	"	"	**	68	40
o	"	"	***	66	40
p	"	"	****	56	35

* Control article, no heat treatment

** 8 hours at 275° F. (135° C.)

*** 8 hours at 300° F. (150° C.)

**** 24 hours at 325° F. (163° C.)

These data show that extended heat treatment does not significantly reduce the polyester-to-rubber adhesion of reinforced elastomeric articles prepared in accordance with the principles of this invention. Each cord of articles a, b, c and d remained completely covered with rubber after being pulled out. In fact, the adhesion retention for polyester cords in these articles is at least as good as that for nylon cords, present standard of the industry. This example also shows that nylon cords have essentially equal adhesion to the two stock formulations specified, whereas

polyester cords in a conventional skim stock of 50/50 natural rubber/styrene - butadiene composition, articles e, f, g and h, exhibit a drastic reduction in adhesion after heating.

The superior performance of polyester cords in the skim stock of Table 1 is due, in part, to the high moisture permeability of that stock, compared to the low permeability of the stock of Table 3. Table 5 shows relative permeability of several rubber stocks. Permeability is determined by using A.S.T.M. Test No. E-96 with the permeability of the stock of Table 1 being the reference point.

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TABLE 5
Relative Rubber Stock Permeability

Stock of Table 1	1
Stock of Table 3	0.25
Conventional chlorobutyl rubber stock	0.05
Stock used for Tire B ₁ in Example I	0.95
Stock used for tire in Example II	0.25

However, high permeability alone appears not to be sufficient. The skim stock used for Tire B₁ has a high relative permeability, but causes a completely unacceptable cord strength loss. This strength loss is apparently due to the use of a sulfenamide accelerator. Sulfenamides, reaction products of 2-mercaptopbenzothiazole and amines such as morpholine, cyclohexylamine, and dimethylamine, are used extensively as accelerators in the rubber industry. It has been found that morpholine is liberated by either homolytic or heterolytic cleavage of a sulfenamide such as 2 - (morpholinothio) - benzothiazole, and furthermore that polyester cords are highly susceptible to degradative attack by morpholine or other volatile amines.

EXAMPLE V

This example further illustrates the effect of moisture permeability and choice of accelerator on retention of adhesion and on cord strength loss, as measured by the laboratory 2-ply pad test.

An adhesive-coated polyethylene terephthalate tire cord of 840/1/2 construction is used to build test pads as described in Example IV in combination with four different rubber stocks having the following compositions:

Rubber stock V-A: A mixture of 75 parts cis - 1,4 - polybutadiene and 25 parts natural rubber with 35 parts FEF black and other con-

ventional compounding agents. One part of 2,2' - dithiobis(benzothiazole) is added as accelerator.

Stock V-B: A styrene/butadiene rubber containing 50 parts FEF black and other conventional compounding agents. The accelerator added is 1.25 parts 2,2' - dithiobis(benzothiazole).

Stock V-C: A mixture of 75 parts cis - 1,4 - polybutadiene and 25 parts natural rubber with 35 parts FEF black and other conventional compounding agents. One part of 2 - (morpholinothio) - benzothiazole is added as accelerator.

Stock V-D: A mixture of 50 parts styrene/butadiene rubber with 50 parts natural rubber and 35 parts HAF black. 1.25 parts 2 - (morpholinothio) - benzothiazole is added as accelerator, along with other conventional compounding ingredients.

For the adhesion test, each pad is aged at 325°F. (163°C.) for 24 hours and then tested at 140°C., as described in Example IV. Stripping tension is compared with that of a similar sample prepared from standard nylon cord and the adhesion results reported as per cent of this nylon control. Strength loss is measured by heating the pad at 325°F. (163°C.) for 24 hours, removing the rubber from a single cord with solvents, and then measuring the breaking strength of the cord in the usual manner at 25°C. The results of the tests are summarized in the following table:

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TABLE 6

Rubber Stock	Moisture Permeability g./m ² /24 hrs.	Approved Accelerator	Retained Adhesion, % of Nylon Control	Cord Strength Loss, %
V-A	34	yes	123	14
V-B	8	yes	23	18
V-C	34	no	43	33
V-D	8	no	18	58

5 An inspection of the data in the table and the compositions of the rubber stock further confirm the fact that both high moisture permeability and proper accelerator are necessary for satisfactory adhesion retention and cord strength retention.

EXAMPLE VI
To further illustrate the criticality of the proper choice of accelerator, tests are carried out using the same basic rubber stock composition but with different accelerators added to separate portions of the stock. Both approved and unacceptable accelerators are used for comparison. The basic rubber stock has the following composition:

TABLE 7

Ingredient	Parts by Weight
cis-1,4-polybutadiene	75
Natural Rubber	25
Zinc Oxide	5
Stearic Acid	2
Processing Oils	8
Carbon Blacks	35
Tackifier	2
Sulfur	2.5
Antioxidant	1
Accelerator	x

20 After adding the designated accelerator, the rubber stock is combined with polyethylene terephthalate tire cord in a laboratory 2-ply test pad of the type described in Example IV, heat aged at 300°F. (150°C.) for 24 hours, and then examined for cord strength loss. The results of the test are shown in the following table:

TABLE 8
Effect of Various Accelerators

Accelerator	Amount phr*	Cord Strength Loss, %
<u>Approved:</u>		
benzothiazole-2-thiol	1	5.6
benzothiazole-2-thiol, zinc salt	1	9.3
tetraethylthiuram-monosulfide	1	4.1
<u>Unacceptable:</u>		
2-(morpholinothio)-benzothiazole	0.7	24
N-cyclohexylbenzothiazole-2-sulfenamide	0.7	19.5
N,N-diisopropylbenzothiazole-2-sulfenamide	0.7	21.8
N-tert.-butylbenzothiazole-2-sulfenamide	0.7	25.1
tetramethylthiuram disulfide	1	78.9

*phr = parts per hundred parts of rubber.

EXAMPLE VII

This example shows that the improvement attained by the proper choice of elastomer permeability and accelerator, in accordance with the principles of this invention, is not limited to the use of one particular adhesive system.

5 Polyethylene terephthalate tire cord samples treated with three different adhesives, and with water only, are tested for adhesion and strength retention in an approved rubber stock and in an unacceptable rubber stock, using the laboratory pad test described in Example IV. The approved rubber stock, Stock VII-A, has the same formulation as that shown in Table 1 with the exception that zinc stearate is used in place of stearic acid. The moisture permeability of this stock is 34 gms. 10 per square meter per 24 hours. The unacceptable rubber stock, Stock VII-B, has the composition shown in Table 3, and shows a moisture permeability of 8 grams per square meter per 24 hours.

15 25 The cord samples are prepared as follows:

(1) Sample 1 is treated with adhesive system A, which is the same as that described in Example I.

(2) Sample 2 is treated with adhesive system B, which involves the application of a subcoat and a topcoat as follows:

Subcoat Composition
34.4% 2-pyrrolidone
6.9% polyepoxide (same as Example I)
16.5% of 37% formaldehyde
1.1% of 10% sodium hydroxide
41.1% water

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This subcoating mixture is applied to the cord, cured, and then overcoated with an RFL mixture prepared as follows:

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Topcoat. A resin master is prepared by mixing 11 parts water, 5.5 parts resorcinol and 2.98 parts 37% formaldehyde. 19.48 parts of this resin master is mixed with 35.76 parts of a 41% solids butadiene/styrene/vinyl pyridine (70/15/15) copolymer latex. The mixture is aged 4 days at room temperature before using.

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(3) Sample 3 is treated with adhesive system C, which involves the application of a subcoat and a topcoat as follows:

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Subcoat. The subcoating mixture consists of 1 part piperazine hydrate and 10 parts of the polyepoxide described in Example I dispersed in a 50/50 mixture of methylene chloride and coconut oil, with a total solids content of approximately 20%. This mixture is applied to the cord, cured, and then overcoated with an RFL mixture which is similar to that used in adhesive system B with the

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exception that it is diluted with water to a concentration of 20% solids.

5 (4) Sample 4 is treated with water only and coded "Adhesive D". This sample shows, by comparison, the negligible effect of the adhesives upon cord strength.

The adhesive-treated cords are incorporated in rubber pads, heat aged, and tested for strength as previously described. The results of the tests are shown in the following table:

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TABLE 9

2-Ply Pad Tests Using Various Adhesives

Sample	Adhesive System	Adhesion at 140° C., lbs.		Cord Strength Loss, %	
		Original/Heat Aged	Rubber Stock VII-A	Rubber Stock VII-B	Rubber Stock VII-A
1	A	65/43	69/6	14	58
2	B	58/59	27/6	19	60
3	C	14/19	13/6	28	45
4	D (water)	5/4	7/5	24	57

15 Test pads for adhesives A, B and D were heat aged at 325°F. (163°C.) for 24 hours. Pads for adhesive C were heat aged at 300°F. (150°C.) for 24 hours before testing. The data clearly show that for each adhesive the combination of polyester cord with approved rubber stock VII-A is superior to the combination of cord with comparative rubber stock VII-B.

EXAMPLE VIII

20 This example illustrates that the total elastomer environment has an effect upon polyester-to-rubber adhesion and upon polyester cord strength loss. It shows that not only does the use of the proper skim stock give improved performance, but also that even better performance is obtained if the proper elastomer composition is used throughout the article.

25 30 A series of rubber stocks are prepared having different moisture permeability ratings and with different accelerators added. These rubber stocks are used in various combinations to prepare laboratory 2-ply test pads reinforced with polyethylene terephthalate tire cord. In some instances only the skim stock

35 is the approved type, while in others both the skim stock and the outer layers of rubber are of the approved type. The pads are heat-aged for 24 hours at 325°F. (163°C.) and then examined for adhesion retention and for cord strength loss. The results are presented in Table 10. Adhesion retention is given in terms of percentage of nylon adhesion, as determined from similar pads prepared with nylon cord and treated in the same manner.

40 45 Various combinations of skim stock and tread stock are also used to prepare a series of 8.50-14, 4-ply pneumatic tires reinforced with polyethylene terephthalate tire cords. The tires are heat-aged for 24 hours at 325°F. (163°C.) and then examined for cord strength loss. The results are shown in Table 11.

50 55 The results in Tables 10 and 11 clearly show that improved performance is obtained by the use of high-moisture-permeability elastomer along with the proper accelerator in the skim stock, and that even greater improvement is obtained if the layers of rubber further away from the cord are also of the approved type.

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TABLE 10
Pad Test: Heat Aging

Sample	Skim Stock			Outer Layers			Adhesion Retained % of Nylon	Cord Strength Loss, %
	Elastomer (Parts)	Accelerator	Permeability g./m ² /24 hrs.	Elastomer (Parts)	Accelerator	Permeability g./m ² /24 hrs.		
A	PBR, 75 NR, 25	2,2'-D	34	PBR, 75 NR, 25	2,2'-D	34	123	14
B	SBR, 100	"	8	SBR, 100	"	8	23	18
C	PBR, 75 NR, 25	"	34	SBR, 50 NR, 50	2-M	8	103	26
D	PBR, 75 NR, 25	2-M	34	PBR, 75 NR, 25	2-M	34	43	33
E	SBR, 50 NR, 50	2-M	8	SBR, 50 NR, 50	2-M	8	18	58

(For codes see Table 11)

TABLE 11
Tire Test: Heat Aging

Sample	Skim Stock			Tread Stock			Cord Strength Loss, %
	Elastomer (Parts)	Accelerator	Permeability g./m ² /24 hrs.	Elastomer (Parts)	Accelerator	Permeability g./m ² /24 hrs.	
F	PBR, 75 NR, 25	2,2'-D	34	PBR, 75 NR, 25	2,2'-D	34	12
G	SBR, 100	2,2'-D	8	SBR, 100	2,2'-D	8	11
H	PBR, 75 NR, 25	2,2'-D	34	PBR, 25 SBR, 75	N-tert.B	10	25
I	PBR, 75 NR, 25	2-M	34	PBR, 75 NR, 25	2-M	34	39
J	SBR, 50 NR, 50	2-M	8	PBR, 25 SBR, 75	N-tert.B	10	44

Codes:

Elastomer

PBR — cis-1,4-polybutadiene
SBR — styrene/butadiene
NR — natural rubber

Accelerator

2,2'-D — 2,2'-dithiobis(benzothiazole)
2-M — 2-(morpholinothio)-benzothiazole
N-tert.B — N-tert.-butylbenzothiazole-2-sulfenamide

Useful elastomeric articles provided by this invention include pneumatic tires for automobiles, trucks, aircraft, etc., and conveyor belts, V-belts, reinforced hoses, and the like.

5 **WHAT WE CLAIM IS:—**

1. A reinforced elastomer article comprising an elastomer and linear condensation polyester fibres, the elastomer having a moisture permeability of at least 20 grams per square meter
- 10 in 24 hours and containing an amine-free accelerator not capable of generating amines under vulcanization conditions.
- 15 2. An elastomer article according to Claim 1, characterized in that the polyester fibres are bonded in a skim stock compounded of elastomer which is a blend of at least 50 per cent by weight of *cis*-1, 4-polybutadiene and up to 50 per cent by weight of rubber.
- 20 3. An elastomer article according to claim 2, wherein the rubber in the elastomer blend is natural rubber.

4. An elastomer article according to claim 2, wherein the rubber in the elastomer blend is styrene-butadiene rubber.

5. An elastomer article according to any of claims 1 to 4 wherein the accelerator is 2,2'-dithiobis (benzothiazole).

6. An elastomer article according to any of claims 1 to 4 wherein the accelerator is a benzothiazole - 2 - thiol.

7. An elastomer article according to any of claims 1 to 4 wherein the accelerator is tetraalkylthiuram monosulfide.

8. Elastomer articles in accordance with Claim 1 substantially as hereinbefore described with reference to the Examples.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
 Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
 copies may be obtained.

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